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The Bryn Mawr College Monographs will be issued in two series; the first, the **Monograph Series,** containing articles that appear here for the first time; the second, the **Reprint Series,** containing reprints of articles that have appeared in other journals.

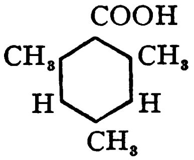
It is proposed to publish these monographs in separate numbers at irregular intervals as material is accumulated. The numbers will be combined into volumes of about 500 pages.

The monographs are edited by a committee of the Faculty of Bryn Mawr College, consisting at present of President M. Carey Thomas, ex-officio, Professor Thomas Hunt Morgan (chairman), Professor Charlotte Angas Scott, and Professor Herbert Weir Smyth.

THE POLYBASIC ACIDS OF MESITYLENE

The polybasic acids of the higher homologues of benzene form a field to a great extent unexplored. Of the acids theoretically possible, the most interesting are those derived from mesitylene and the durenes by the introduction of carboxyl groups in place of the hydrogen of the nucleus. In the case of these hydrocarbons, however, only one carboxyl group has so far been introduced. Of the sixteen possible acids derived from mesitylene by successively replacing ring hydrogen atoms with carboxyl groups and subsequently oxidizing the various methyl groups, only five are known.

The object of the following investigation was to prepare and study the three acids derived from mesitylene by replacing the hydrogen atoms of the nucleus with one, two, and three carboxyl groups. The simplest of these acids, mesitylene carbonic acid,



has already been described. It was first prepared in pure condition by Jacobsen,[1] who oxidized isodurene with dilute nitric acid and got a mixture of acids. One of these, "β-isodurylic acid," with a melting point of 151°, is identical with mesitylene carbonic acid. Claus[2] prepared it later from acetylmesitylene,

$$C_6H_2(CH_3)_3COCH_3,$$

which he oxidized with dilute alkaline permanganate to the corresponding glyoxylic acid, $C_6H_2(CH_3)_3COCOOH$, and then oxidized this further to the mesitylene carbonic acid. Feith,[3] by heating mesitylene glyoxylic acid in a stream of carbon dioxide, obtained among other substances the same mesitylene carbonic acid. Its acid amide was prepared by Gattermann[4] by treating mesitylene with chlor carbonic amide, $ClCONH_2$, and aluminium chloride.

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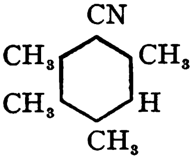
[1] Berichte, 15, 1855.

[2] Journ. f. prak. Chem. [2], 41, 506.

Historically, mesitylene carbonic acid is interesting as the substance whose failure to give an ester when treated with alcohol and hydrochloric acid, first led to a systematic study of di-ortho-substituted compounds and their peculiarities. Victor Meyer,[5] wishing to make its ester, tried the above-mentioned process, but got so poor a yield that he investigated the cause of the difficulty. After examining a large number of similarly substituted acids, he was led to enunciate his "Ester Law"—that those aromatic acids in which the two positions ortho to the carboxyl group are occupied by substituents other than hydrogen, when treated with alcohol and hydrochloric acid in the cold, give esters in very small quantity or not at all. Conversely, he found[6] that the esters of such acids, when made by the action of an alkyl halide on their silver salts, are saponified with great difficulty.

Several instances of abnormal behavior in di-ortho-substituted compounds had been recorded before this work of Meyer's, but he first pointed out the cause, and laid down the general principle that di-ortho-substitution profoundly affects the reactivity of any group. For example, A. W. Hofmann[7] had found that he could not saponify a nitrile of isodurene,



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[3] Berichte, 24, 3544.

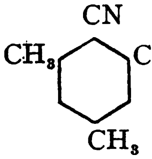
[4] Liebig's Ann., 244, 55.

[5] Berichte, 27, 510. Cf. also, Berichte, 27, 1581 and 3146; Berichte, 28, 182, 3197.

[6] Berichte, 28, 1262.

[7] Berichte, 17, 1914.

Küster and Stallberg,[8] also, had made the nitriles of mesitylene mono-, di-, and tri-carbonic acids,



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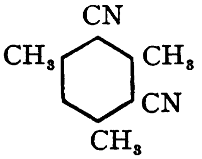
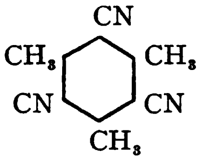
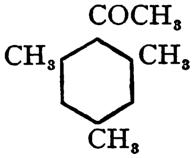


and



but could not convert any of them into the acids by saponification. Di-ortho-substituted nitriles are, in general, very difficult to saponify. The process is not impossible, however, as is shown by the fact that the nitrile of mesitylene carbonic acid has been converted into the acid[9] by boiling for 72 hours with concentrated alcoholic caustic potash, and diazotizing the resulting acid amide by Bouveault's method.[10] Acid amides and also acid chlorides, when di-ortho-substituted, were found by Meyer and his pupils to be surprisingly stable. For example,[11] o, o, di-iodo-benzoyl chloride can be boiled with sodium hydroxide solution without much decomposition.

Many other carboxyl compounds, such as mixed ketones, when di-ortho-substituted, exhibit an inertness similar to the acids and nitriles. Substances of the type of acetyl mesitylene,



give no oximes or hydrazones.[12] Klages[13] also has shown that such di-ortho-substituted ketones give no addition product in the normal way with phosphoric acid. Instead, the ketone group is split off, leaving a hydrocarbon.

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[8] Liebig's Ann., 278, 219.

[9] Berichte, 29, 834, footnote.

[10] Bull. Soc. Chim. [2], 9, 368.

[11] Lützens, Berichte, 29, 2838. Cf. V. Meyer, Berichte, 27, 3153; Sudborough, Journ. Chem. Soc., 71, 229.

[12] Berichte, 28, 3207; 29, 830.

[13] Berichte, 32, 1549.

These phenomena V. Meyer explained as a result of the space arrangement of the molecule. Heavy or complicated groups on each side of a carboxyl group, for instance, diminish the latter's reactivity in a way that suggests the analogy of the "damping" of vibrating bodies. This inertness of the di-ortho-substituted group is evident not only in its indifference to reagents, of which cases have been cited above, but also in the comparatively small effect which the presence of such a group has on the molecule as a whole. Certain well-known peculiarities of mesitylene, for instance, can be explained as the effects of di-ortho-substitution, such as the ease with which two or three groups like the nitro group are introduced. One nitro group goes easily into benzene, but once there it makes the introduction of a second group more difficult; while in mesitylene the first nitro group has so little inhibiting effect that it is practically impossible to stop nitration at the point where only one group has entered.

A more remarkable example of this is that although only *one* acyl group can be introduced into benzene, toluene and other hydrocarbons, by the action of an acyl chloride and aluminium chloride, *two* such groups can be introduced into mesitylene, durene and isodurene by the same reaction.[14] Ordinarily an acyl group "protects" the remaining hydrogen atoms from further action of the reagents; but the first acyl group to enter mesitylene or the durenes is necessarily di-ortho-substituted and consequently inert, and a second group can then be made to enter the molecule. In the case of mesitylene, it has been found that even a *third* group can be introduced by sufficiently energetic means. E. Louïse[15] succeeded in getting successively one, two and three benzoyl groups into mesitylene, the latter by using a large excess of benzoyl chloride and heating to 198° for several hours. But as yet no one has succeeded in introducing three aliphatic acyl groups into mesitylene.

This account of di-ortho-substitution effects shows that, if the three methods available for introducing carboxyl groups into hydrocarbons—(1) the formation of the nitrile and its subsequent saponification, (2) the introduction of an acid amide or acid chloride group with the help of aluminium chloride, and (3) the introduction and oxidation of a ketone group—the first two can be applied only under very unfavorable conditions when the acid to be formed is di-ortho-substituted. Di-ortho-substitution is in these methods a hindrance, while in the third method it is a help. It favors the introduction of acyl groups to form the necessary ketones and does not interfere with oxidation of these ketones to the desired acids. This last method was, therefore, selected for preparing the acids of mesitylene.

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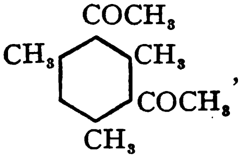
[14] Baum and V. Meyer, Berichte, **28**, 3212; V. Meyer, Berichte, **29**, 846 and 1413.

[15] Ann. Chim. Phys. [6], **6**, 236.

In selecting the acid chlorides suitable for the purpose, benzoyl chloride could not be considered, as Louïse[16] showed that the oxidation of benzoyl mesitylene gave (o) and (p) benzoyl mesitylenic acids; and Mills and Easterfield[17] on oxidizing di-benzoyl mesitylene got two dibenzoyl uvitic acids. An aliphatic acyl group was therefore necessary, and acetyl and chloracetyl chlorides were used.

EXPERIMENTAL.

I. *Di-acetyl mesitylene*, 

, was prepared by V. Meyer's[18] method; but as this method was worked out originally only for small quantities of material, it was found necessary to modify it in some details when working on a larger scale. Meyer comments on the tendency of the diketone to remain oily (it melts at 46° and distils undecomposed at 310°), and it was found that,

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[16] Loc. cit., p. 218.

[17] Proc. Chem. Soc., 15, 22; Chem. Centralbl., 1899, I, 679.

[18] Berichte, 29, 1413.

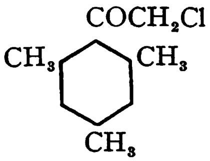
on using fifty grams or more of mesitylene in one operation and adhering strictly to Meyer's directions, so much mono-acetyl mesitylene was always present in the product that it remained liquid even in a freezing mixture. To obtain the diketone in a solid state, the following method has proved highly satisfactory:

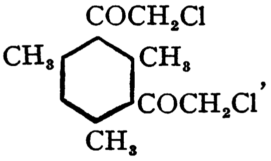
One part (one molecule) of mesitylene is dissolved in from ten to fifteen parts by weight of carbon disulphide in a flask provided with a dropping funnel and a return condenser. Six parts by weight of fresh, finely powdered aluminium chloride is added, and then two parts (about three molecules) of acetyl chloride is allowed to run slowly through the dropping funnel, with an interval of 24 hours between the first and last portions added. If the aluminium chloride is added last, its action on the excess of acetyl chloride present results in relatively large amounts of bye-products such as acetylacetone, and some of the mesitylene is either left unchanged or converted merely into its mono-acetyl derivative. The flask, after all the acetyl chloride has run in, is set *in the direct rays of the sun,* and left to itself for a length of time depending on the weather. In bright winter weather two weeks is a fair average time. The action of sunlight at first accelerates the evolution of gas and finally conditions it absolutely. When no further action is observed in ordinary sunlight, the upper, clear layer of the solvent is poured off and saved for future syntheses. The dark, viscous mass remaining is removed from the flask, and dropped in small portions on cracked ice. The usual method of adding ice to the mixture in the flask is not to be recommended in this case, on account of the large excess of aluminium chloride.

The oil obtained by decomposition with the ice water, is extracted with successive portions of ligroine; the solvent is allowed to evaporate over night and deposits long needles of di-acetyl mesitylene. This is freed from a small amount of dark oil by pressing on a porous plate, when a pale yellow solid is left which melts usually within 3° of the melting point of the pure diketone. This solid instantly induces crystallization of such oily specimens of the diketone as boil above 280°. Once in possession of the solid no difficulty is experienced in purifying even very impure products.

II. In the literature of the subject, there is no record of any attempt to introduce three acetyl groups into mesitylene. It has been found that in experiments where a great excess of acid chloride and aluminium chloride were used, only diketone was obtained. In fact, one very good way to make di-acetyl mesitylene is to dissolve aluminium chloride in acetyl chloride, and drop in mesitylene. On standing in sunlight, crystals of the diketone separate from the liquid, but no triketone has been obtained. Raising the temperature favors the formation of acetylacetone and consequent waste of the acid chloride. It is possible that very prolonged action of sunlight might have the desired result, as one mixture made up in the usual way, after standing for two months in a window facing southwest, was observed to give off gas slowly when the atmosphere was unusually clear. But even if the complete transformation of mesitylene into tri-acetyl mesitylene were possible by this means, the synthesis would require so long a time that it was desirable to seek some other and shorter method for forming a triketone.

Chloracetyl chloride, $ClCH_2COCl$, which boils at 105.5° and shows no tendency to form a condensation product similar to acetylacetone under the action of aluminium chloride, was selected and its action on mesitylene studied.

III. *Mono-chloracetyl mesitylene,* , was described by A. Collet,[19] and is a solid melting at 68.5°.

Di-chloracetyl mesitylene,[20] , was prepared

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[19] Bull. Soc. Chim. [2], 17, 508.

[20] Cf. Berichte, 29, 2567.

in the same way as di-acetyl mesitylene; but in this case, the reaction goes on much more smoothly. One part (one molecule) of mesitylene, three parts (about two and a half molecules) of chloracetyl chloride, fifteen parts of carbon disulphide and six parts of aluminium chloride are mixed (usually in the order given) in a flask that is kept cool with running water. The mixture may be heated at once on a water bath for one or two hours, when the reaction is complete; or it may be left in the cold for 48 hours or more. The solvent is poured off and the product of the reaction decomposed with ice in the same way as di-acetyl mesitylene. The diketone comes out as a grayish solid which is filtered off and washed with dilute hydrochloric acid. From 45 grams of mesitylene, 105 grams of the crude product were gotten. This always contains traces of chloracetophenone, which in one synthesis was gotten in sufficient quantity to be analyzed and identified.[21] For purposes of purification, the product is extracted with ligroine, which readily dissolves chloracetophenone and any monochloracetyl mesitylene that may be formed, but dissolves dichloracetyl mesitylene only to a very small extent. The residue, after extracting twice with ligroine, is crystallized from hot alcohol, from which it comes out in well-formed plates. The last trace of coloring matter and of the odor of chloracetophenone is removed only by boiling the alcoholic solution with animal charcoal.

I. 0.2000 gram substance gave 0.2063 gram AgCl.
II. 0.1592 gram substance gave 0.1658 gram AgCl.

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[21] The substance crystallized well from ligroine, melted at 51°-52°, possessed a sharp, characteristic odor and caused painful irritation of the eyes. The analyses were:

I. 0.22155 gram substance gave 0.2009 gram AgCl.
II. 0.15085 gram substance gave 0.1387 gram AgCl.
III. 0.3180 gram substance gave 0.1435 gram H_2O and 0.7061 gram CO_2.

	Found.		
Calculated for C_8H_7OCl.	I.	II.	III.
Cl 22.9	22.4	22.7	....
C 62.1	....	....	60.5
H 4.5	....	....	5.0

The molecular weight, determined by the freezing point method, using naphthaline as the solvent, was 156.7 as against 154.5, theory.

III. 0.1404 gram substance gave 0.0687 gram H_2O and 0.2966 gram CO_2.

Calculated for $C_{13}H_{14}O_2Cl_2$.		Found. I.	Found. II.	Found. III.
Cl	26.0	25.5	25.8	..
C	57.4	..	..	57.6
H	5.1	..	..	5.4

Di-chloracetyl mesitylene melts at 133°-133.5°. It is not changed when kept for 3 hours at a temperature of 160°-180°. In boiling alcohol it is soluble in the proportion of 98 parts per 1000; in alcohol at 21°, in the proportion of 5.5 parts per 1000. Ether dissolves 26 parts per 1000, and on evaporating leaves it in transparent crystals 2-3 mm. in diameter. The diketone is insoluble in water, nearly insoluble in ligroine, easily soluble in benzene, acetone and other organic solvents. It also dissolves in concentrated sulphuric and nitric acids in the cold, and is reprecipitated unchanged when the solutions are diluted with water.

Like other di-ortho-substituted diketones, di-acetyl mesitylene gives no oxime, hydrazone or acid sulphite addition product. On the other hand, contrary to the observation of Klages[22] that di-ortho-substituted ketones are converted into hydrocarbons by syrupy phosphoric acid, this diketone, heated with phosphoric acid, does not give mesitylene. An excess of syrupy phosphoric acid and 5 grams of the diketone was heated in a flask with a return condenser. The ketone melted (the temperature was about 140°) and a sublimate of diketone was formed in the upper part of the flask and clogged the condenser, which interfered somewhat with the course of the experiment. After heating for several hours, some of the mixture was diluted and subjected to distillation with steam. No mesitylene or any other volatile substance was obtained. On account of the difficulty due to the sublimation of the diketone, the same mixture was removed from the flask to a tube, sealed up, and heated to 150° for 15 hours;

[22] See above. Klages obtained mesitylene from di-acetyl mesitylene.

but again no trace of mesitylene could be obtained on distilling with steam. The diketone was recovered unchanged.

Though di-acetyl mesitylene is a perfectly neutral substance, di-chloracetyl mesitylene, probably on account of the chlorine atoms next its carboxyl groups, possesses very weak acid properties. It dissolves in alcoholic caustic potash with a deep red color, and water, which precipitates it from its solution in ordinary alcohol, does not precipitate it from the alkaline solution. It gives, however, no color reaction with ferric chloride. V. Meyer[28] suggested that di-acyl mesitylenes, which are necessarily 1-5 diketones, might give condensation products analogous to those obtained by Knoevenagel and others from open chain 1-5 diketones. Meyer's efforts to condense di-acetyl mesitylene were fruitless; but in the hope that the chlorine atoms would make the ketone groups of di-chloracetyl mesitylene more reactive than those in di-acetyl mesitylene, various attempts were made to condense the chlor ketone to a double ring compound. Iodine in alcoholic potash, hydroxylamine, alcoholic ammonia, finely divided silver, metallic sodium in absolute ether, aniline, etc., were tried, but entirely in vain. The ketone was recovered unchanged in most cases, but in others oily or tarry decomposition products were obtained.

IV. *Attempts to prepare tri-chloracetyl mesitylene.*—In one experiment, 1 gram di-chloracetyl mesitylene, 0.5 gram chloracetyl chloride, 15 grams carbon disulphide and 12 grams freshly distilled aluminium chloride were heated for two hours on a water bath and the product isolated in the usual way. 1 gram of unchanged diketone was recovered.

In a second experiment, 0.5 gram chloracetyl chloride was dissolved in 400 cc. carbon disulphide, and freshly distilled aluminium chloride was added to it as long as it would dissolve at the boiling point of the solvent. This was then added to a hot solution of 1 gram di-chloracetyl mesitylene in carbon disulphide and the whole heated on a water bath for several hours. It was hoped that the reaction could be brought about by having all the substances in solution, but the diketone was recovered in nearly quantitative amount. A small amount of tarry decomposition product was formed.

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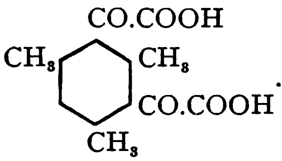
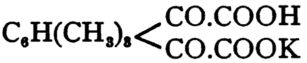
[28] Berichte, 29, 1414.

Chloracetyl chloride was next used as a solvent, both on account of its relatively high boiling point and its holding the addition product of the acyl chloride and aluminium chloride in solution. When mesitylene is added to a solution of aluminium chloride in chloracetyl chloride, crystals of di-chloracetyl mesitylene separate out in the cold, but no tri-chloracetyl derivative is gotten. When di-chloracetyl mesitylene is heated with the solution the main product is a thick black oil, which can not be made to solidify. Some of the diketone is recovered unchanged.

The action of sunlight was tried on a mixture of mesitylene and the corresponding reagents made up in the usual way, but with a large excess of chloracetyl chloride. The effect was much less than in the case of acetyl chloride; the evolution of gas was slower and ceased altogether after about two months.

V. *Mesitylene di-glyoxylic acid*,  .—Di-acetyl mesitylene was weighed out in portions of 10 grams each into 4-litre bottles, which contained each a solution of 31 grams potassium permanganate and 17 grams potassium hydroxide in 4 litres of water. The bottles were stoppered and shaken frequently. Oxidation began at once and after 48 hours the solution was usually colorless, while a heavy precipitate of manganese di-oxide had formed. If necessary, the last traces of color were removed by running sulphur dioxide through the solution. The liquid was then filtered and acidified with sulphuric acid. In order to prevent possible hydrolysis of the keto-acid during the evaporation of the very dilute solution, the liquid was neutralized with barium carbonate, boiled and again filtered. The neutral solution was then evaporated until the inorganic salts present began to crystallize out in the cold, when more sulphuric acid was added. A violent evolution of gas took place, and a yellowish crystalline solid separated out, which was filtered off and recrystallized from boiling water. This substance, as is shown by the analyses given below, is the acid potassium salt of mesitylene di-glyoxylic acid,  $C_6H(CH_3)_3<\begin{smallmatrix}CO.COOH\\CO.COOK\end{smallmatrix}$ To prepare the free acid from it, a supersaturated solution of it was made in water and treated with about one-fifth its volume of concentrated sulphuric acid. On cooling, a yellow oil separated out and then long white needles. The oil finally solidified and the whole was filtered. Some crystals were saved and the rest redissolved in hot water, and on cooling was induced to crystallize without separation of oil by dropping in one of these crystals. The recrystallization was repeated twice and the acid dried on filter paper in the air.

I. 0.3503 gram acid gave 0.1671 gram H_2O and 0.6631 gram CO_2.

II. 0.2076 gram acid gave 0.1000 gram H_2O and 0.3921 gram CO_2.

Calculated for $C_{13}H_{12}O_6.2H_2O$.		Found.	
		I.	II.
C	52.0	51.6	51.5
H	5.3	5.3	5.3

0.5089 gram air-dried acid lost at 40°-45°, 0.0298 gram; at 55°-58°, 0.0309 gram.

Total loss in weight 0.0607 gram.

Calculated loss for $2H_2O$, 0.0611 gram.

The crystals of mesitylene di-glyoxylic acid possess no definite melting point, as they begin to give off water of crystallization at 40° and are completely liquid at 100° only. A melted specimen, cooled rapidly, melted again from 90° to 130°. When dried, as above, at 58°, the substance can be heated to 150° without melting or losing weight, but at that temperature it begins to decompose, partly sublimes and then loses weight. The acid is very readily soluble in hot water, and pure specimens crystallize from the solution in white needles with a silky lustre, 1-1.5 cm. long. It is insoluble in carbon disulphide and ligroine, more or less readily soluble in other ordinary solvents. It crystallizes well from ether on adding ligroine, and allowing the solution to evaporate slowly. Good crystals are also formed from hot benzene.

This acid can be prepared from di-chloracetyl mesitylene as well as from di-acetyl mesitylene, by oxidation with alkaline permanganate. The chlorketone, however, oxidizes more slowly, requiring 8 to 10 days. The substances were mixed in the following proportions: 12.5 grams of di-chloracetyl mesitylene, 18.4 grams of permanganate, 7.5 grams of caustic soda and 2.5 litres of water. The acid was isolated by extracting the filtered and acidified solution six times with ether. The oil left on evaporating the ether solidified on standing and was identical with the other specimens of mesitylene di-glyoxylic acid.

Of the salts of this di-glyoxylic acid, the acid potassium salt is the most characteristic. It is precipitated whenever a moderately concentrated solution of the acid in caustic potash is acidified with sulphuric acid. Pure white crystals may be obtained by recrystallizing from hot water, adding animal charcoal.

I. 0.2100 gram substance gave 0.0595 gram K_2SO_4.

II. 0.4666 gram substance gave 0.1333 gram K_2SO_4.

Calculated for $C_{13}H_{11}O_6K$.		Found.	
		I.	II.
K	12.9	12.7	12.8

The salt dissolves in dilute soda solution, evolving carbon dioxide, and is reprecipitated by acids. It dissolves slowly in hot water, but forms a very concentrated solution, from which it crystallizes slowly on cooling. It is often necessary to rub the vessel with a rod to start crystallization. The crystals are thick prisms, 1 mm. or so in length, which melt above 300° and burn with a violet flame.

The neutral salts are much more easily soluble than the acid salts. The neutral barium salt, however, can be made by treating the free acid with barium carbonate, and it crystallizes from hot, concentrated solution.

Analysis:

	Calculated for $C_{13}H_{16}O_9Ba$.	Found.
Ba	29.15	29.05
$3H_2O$	11.75	11.80

Analysis of anhydrous salt:

	Calculated for $C_{13}H_{10}O_6Ba$.	Found.
Ba	33.05	33.04

The "Ester Law" affects only those aromatic acids in which the carboxyl group is directly attached to the benzene ring. Mesitylene di-glyoxylic acid should, therefore, give an ester with alcohol and hydrochloric acid, and it was found to do so. The di-methyl ester was prepared by E. Fischer's method,[24] by boiling the acid for five hours in a solution of 3 per cent of hydrochloric acid in absolute methyl alcohol. From 8.5 grams of acid, 5 grams of ester was obtained, and 3 grams of acid recovered. The ester crystallizes in colorless octahedra both from ether and methyl alcohol.

0.2223 gram substance gave 0.1093 gram H_2O and 0.4983 gram CO_2.

	Calculated for $C_{15}H_{16}O_6$.	Found.
C	61.64	61.17
H	5.48	5.46

The ester melts at 103.5°-104.5°. It is readily saponified to the acid. The di-ethyl ester, made in the same way, is an oil and was not further examined. The maximum yield of ester in both cases was about 60 per cent. According to V. Meyer, mesitylene mono-carbonic acid gives 90 per cent of ester by this method.

Claisen[25] found that phenylglyoxylic acid gave a color reaction with benzene and concentrated sulphuric acid. Probably, on account of the di-ortho-substitution, mesitylene di-glyoxylic acid gives no such test. Neither does it give an acid sulphite addition product, and its ester does not give a hydrazone.

That mesitylene di-glyoxylic acid is a very strong acid is shown by the fact that its acid potassium salt crystallizes from dilute sulphuric acid; but especially by its very high dissociation constant, as given below. Its electrical conductivity was measured by the method given in Ostwald's "Physico-Chemical Measurements." For purposes of comparison, mesitylene mono-glyoxylic acid, prepared by the method of Claus,[26] was also measured and its dissociation constant determined. The mono-glyoxylic acid used was crystallized from water, from which it was deposited as transparent yellow octahedra about 2 mm. long, with a melting point of 115°.

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[24] Berichte, 28, 3252.

[25] Berichte, 12, 1505.

The temperature at which all the conductivity measurements in this paper were made was 25°. The apparatus was all carefully calibrated. The water used in the first measurements was purified by partial freezing and had a specific conductivity of 1.4×10^{-6}. That used in the later measurements was purified by distillation and had an average specific conductivity of 2.2×10^{-6}. The constant of the cell was 129.9.

TABLE I.

Mesitylene Mono-Glyoxylic Acid.

$\mu \infty = 360.7$

v	*w*	*a*	*b*	*μ*	*av. μ*	*d*	100 *k*
32	15 20	47.7 55.6	52.3 44.4	252.7 260.2	256.45	....	5.47
64	25 30	46.7 51.0	53.3 49.0	291.4 288.5	290.45	34.00	5.19
128	50 55	48.8 50.9	51.2 49.1	316.9 314.4	315.65	25.20	4.84
256	80 100	44.5 50.3	55.5 49.7	333.3 336.5	334.90	19.35	4.75
512	180 210	48.6 52.5	51.4 47.5	349.3 350.1	349.70	14.80	6.12
1024	350 400	48.5 52.0	51.5 48.0	357.8 360.2	359.00	9.30	19.30
2048	700 750	49.3 51.1	50.7 48.9	369.5 371.4	370.45	9.45	....
4096	1200 1500	45.6 51.7	54.4 48.3	371.6 388.6	380.10	9.65	....

K = 5.27

[26] Loc. cit.

TABLE II.

Sodium Salt of Mesitylene Mono-Glyoxylic Acid.

v	*w*	*a*	*b*	*μ*	*av. μ*	*d*
16	40 30	53.9 46.4	46.1 53.6	60.7 60.0	60.35	....
32	60 70	47.9 51.8	52.1 48.2	63.7 63.8	63.75	3.40
64	100 130	43.9 50.9	56.1 49.1	65.1 66.3	65.70	1.95
128	230 250	49.1 51.1	50.9 48.9	69.7 69.5	69.60	3.90
256	450 500	49.7 52.3	50.3 47.7	73.0 72.9	72.95	3.35
512	800 1000	47.6 53.6	52.4 46.4	75.5 76.8	76.05	3.10
1024	1500 1800	48.0 52.7	52.0 47.3	80.0 80.5	80.25	4.20

$\mu_\infty = 84.75$

TABLE III.

Mesitylene di-Glyoxylic Acid.

$\mu_\infty = 371$

v *	*w*	*a*	*b*	*μ*	*av. μ*	*d*	100 *k*
16	8 10	47.2 52.7	52.8 47.3	226.9 231.5	229.2	....	6.23
32	17 15	51.5 48.5	48.5 51.5	259.6 260.9	260.2	31.0	5.13
64	25 30	46.5 51.1	53.5 48.9	289.0 287.6	288.3	28.1	4.23
128	50 55	48.5 51.0	51.5 49.0	313.9 315.3	314.6	26.3	3.69
256	90 100	47.5 50.2	52.5 49.8	342.1 335.2	338.6	22.0	3.50
512	170 190	47.2 50.1	52.8 49.9	357.9 351.4	354.9	16.3	....
1024	350 370	49.8 51.2	50.2 48.8	377.0 377.3	377.1	23.2	....
2048	700 750	49.8 51.6	50.2 48.4	369.0 362.8	365.9	−11.2	....
4096	1300 1500	48.1 51.7	51.9 48.3	379.3 379.7	379.5	13.6	....

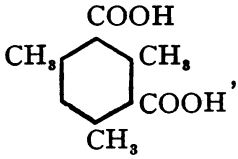
* *v* = volume of 1 gram *equivalent.*

TABLE IV.

Sodium Salt of Mesitylene di-Glyoxylic Acid.

v	*w*	*a*	*b*	*μ*	*av. μ*	*d*
32	50 60	46.8 51.4	53.2 48.6	73.12 73.26	73.19	....
64	100 110	47.8 50.2	52.2 49.8	76.09 76.19	76.14	2.95
128	200 210	49.0 50.3	51.0 49.7	80.05 80.32	80.18	4.04
256	400 420	49.9 51.2	50.1 48.8	82.80 83.29	83.05	2.87
512	750 800	49.2 50.9	50.8 49.1	85.89 86.17	86.06	3.01
1024	1400 1500	48.4 50.3	51.6 49.7	89.12 89.75	89.42	3.26

$\mu_\infty = 95.42$

VI. *Mesitylene di-carbonic acid,* , is formed when mesitylene di-glyoxylic acid is oxidized with acid permanganate solution. The yield is, at best, about 70 per cent of the theoretical, and is considerably lower unless proper precautions are taken. Of a number of experiments carried out under different conditions, the following gave the best results: 2.4 grams of mesitylene di-glyoxylic acid was dissolved in 500 cc. of water and 10 cc. of concentrated sulphuric acid was added. The temperature was about 10°. A solution of the calculated amount of potassium permanganate (1.0 gram) was then added through a dropping funnel whose end had been drawn out to a fine point so that it required half an hour for all the liquid to flow through. It was found desirable to keep the tip of the funnel under the surface and to move it about, and also to stir constantly. The reason for this was that the permanganate acted instantly on the di-glyoxylic acid, and unless it was distributed well as it entered the reaction vessel, it was apt to oxidize part of the material too far. The solution became cloudy during the oxidation; but after standing over night, it was warmed to get rid of carbon dioxide, and the suspended matter dissolved. On cooling, the solution was extracted several times with ether, and the latter, on evaporating, left 1.2 grams of oxidation product.

The mesitylene di-carbonic acid from several oxidations, carried out in much the same way as the above, was first purified by taking advantage of the fact that, as a di-ortho-substituted acid, its ester is formed with much greater difficulty than the esters of the di-glyoxylic acid and any other acids not di-ortho-substituted that might be present.[27] The crude acid was therefore boiled for 5 hours with a 3 per cent solution of hydrochloric acid in absolute alcohol, by which process the esters of the other acids were formed, while the mesitylene di-carbonic acid was recovered as such.[28] Its melting point had risen from 255°-259° to 264°-270°. As it was still impure, it was again subjected to the same esterification process, but without any further effect on the melting point. One such treatment evidently removes all the acids present that are easily converted into esters. The removal of the remaining impurities was effected to some extent by dissolving the acid in dilute soda solution, and extracting seven times with ether, which took out a small quantity of oily substance. The acid was then precipitated from the soda solution by sulphuric acid, and was finally recrystallized from a large quantity of hot water. The first crop of crystals was discarded and the filtrate concentrated to about half its volume. The second crop of crystals were still impure and melted in the neighborhood of 265°; but the filtrate from these on further evaporation, deposited white microscopic crystals of pure mesitylene di-carbonic acid, and this last product was dried and analyzed.

[27] Cf. V. Meyer and Sudborough, Berichte, 27, 1581.

[28] V. Meyer, Berichte, 28, 2774.

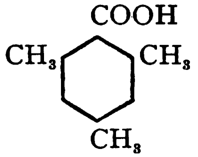
I. 0.2133 gram acid gave 0.4930 gram CO_2 and 0.1076 gram H_2O.

II. 0.1018 gram acid gave 0.2321 gram CO_2 and 0.0536 gram H_2O.

Calculated for $C_{11}H_{12}O_4$.		Found. I.	Found. II.
C	63.4	63.0	63.2
H	5.77	5.60	5.85

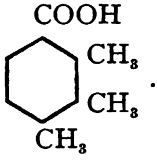
Mesitylene di-carbonic acid melts at 283° with decomposition. It is easily soluble in hot water and in the ordinary organic solvents. From a concentrated solution in water, it is deposited as a crystalline powder, but on coming down from a more dilute solution, it forms hemispherical crystalline aggregates, usually slightly yellow. As a di-ortho-substituted acid, it was found to obey V. Meyer's "Ester Law." From 2.0 grams of acid there was obtained by E. Fischer's esterification method 0.045 gram of an oily ester—*i. e.*, 2.3 per cent of the theoretical amount.

The electrical conductivity and the dissociation constant of mesitylene di-carbonic acid were determined in the same way as in the case of the glyoxylic acids as given above. For the sake of comparison, and also for its independent interest, measurements were also made of mesitylene mono-carbonic acid,



,

and one of its isomers, prehnitylic acid,



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Since the latter is not di-ortho-substituted, but has the same number of methyl groups, it serves to give some standard by which to estimate the effect of the di-ortho-substitution. It is extremely difficultly soluble in water, so that measurements could be conducted only in very dilute solutions. The same difficulty occurs, but to a smaller extent, in the case of mesitylene monocarbonic acid.

TABLE V.

PREHNITYLIC ACID, M. PT. 165°.

$\mu\infty = 351$

v	*w*	*a*	*b*	*μ*	*av. μ*	*d*	100 *k*
512	1500 1600	50.0 51.6	50.0 48.4	44.34 44.32	44.33	....	.00354
1024	2200 2100	50.2 49.1	49.8 50.9	60.95 61.11	61.03	16.70	.00373
2048	3000 3200	48.6 50.4	51.4 49.6	81.92 82.22	82.07	21.04	.00293
4096	5000 4500	51.7 49.1	48.3 50.9	113.9 114.0	113.95	31.88	.00378

K = .00349

TABLE VI.

SODIUM SALT OF PREHNITYLIC ACID.

v	*w*	*a*	*b*	*μ*	*av. μ*	*d*
32	65 70	48.7 50.5	51.3 49.5	60.70 60.57	60.63	....
64	120 140	47.4 51.5	52.6 48.5	62.43 63.07	62.75	2.12
128	240 260	48.2 50.5	51.8 49.5	64.63 65.37	65.00	2.25
256	470 500	48.6 50.3	51.4 49.7	66.88 67.30	67.09	2.09
512	900 1000	48.2 51.1	51.8 48.9	68.76 69.50	69.13	2.04
1024	1800 1900	48.9 50.4	51.1 49.6	70.72 71.12	70.92	1.79

$\mu\infty = 75$

TABLE VII.

Mesitylene Mono-Carbonic Acid, m. pt. = 150.5°–151°.

$\mu_\infty = 352$

v	*w*	*a*	*b*	*μ*	*av. μ*	*d*	100 *k*
128	220	47.6	52.4	68.82	69.24	....	.0376
	250	51.1	48.9	69.66			
256	350	49.8	50.2	94.22	94.26	25.02	.0382
	370	51.2	48.8	94.30			
512	520	49.2	50.8	123.9	123.9	29.6	.0373
	550	50.6	49.4	123.9			
1024	770	48.1	51.9	160.1	160.2	36.3	.0371
	820	49.7	50.3	160.3			
2048	1200	47.5	52.5	195.9	196.7	36.4	.0346
	1300	49.7	50.3	197.6			
4096	2000	47.8	52.2	243.6	239.6	42.9	....
	2100	48.1	51.9	234.8			

K = .0375

TABLE VIII.

Sodium Salt of Mesitylene Mono-Carbonic Acid.

v	*w*	*a*	*b*	*μ*	*av. μ*	*d*
32	65	49.1	50.9	61.68	61.49	....
	70	50.8	49.2	61.30		
64	120	47.8	52.2	63.43	63.63	2.14
	140	51.8	48.2	63.83		
128	220	46.4	53.6	65.57	65.72	2.09
	250	49.7	50.3	65.81		
256	450	47.8	52.2	67.66	67.75	2.03
	500	50.5	49.5	67.85		
512	900	48.5	51.5	69.60	69.82	2.07
	1000	51.3	48.7	70.04		
1024	1800	49.5	50.5	72.44	72.36	2.54
	1900	50.8	49.2	72.28		

$\mu_\infty = 76.4$

TABLE IX.

MESITYLENE DI-CARBONIC ACID, M. PT. 283°.

$\mu\,\infty = 373$

v	w	a	b	μ	$av.\ \mu$	d	$100\ k$
64	100 110	49.8 52.1	50.2 47.9	82.47 82.20	82.34	....	.0977
128	150 170	48.1 51.2	51.9 48.8	102.9 102.9	102.9	20.6	.0821
256	250 280	48.6 51.6	51.4 48.4	125.9 126.6	126.3	23.4	.0676
512	400 440	47.6 50.2	52.4 49.8	151.0 152.4	151.7	25.4	.0544
1024	700 750	48.6 50.4	51.4 49.6	179.6 180.5	180.0	28.3	.0460
2048	1200 1300	48.6 50.8	51.4 59.2	204.5 206.5	205.2	25.2	.0328
4096	2000 2200	47.7 50.2	52.3 49.8	242.6 243.8	243.2	38.0	....

K = .0977 (?)

TABLE X.

SODIUM SALT OF MESITYLENE DI-CARBONIC ACID.

v	w	a	b	μ	$av.\ \mu$	d
32	60 55	50.3 48.1	49.7 51.9	70.10 70.02	70.06	....
64	100 110	46.8 49.4	53.2 50.6	73.13 73.76	73.45	3.39
128	190 220	46.7 50.7	53.3 49.3	76.84 77.91	77.41	3.96
256	400 420	49.4 50.8	50.6 49.2	81.14 81.75	81.44	4.03
512	750 780	49.2 50.2	50.8 49.8	85.89 85.96	85.93	4.49
1024	1400 1500	48.5 50.3	51.5 49.7	89.48 89.74	89.54	3.61

$\mu\,\infty = 97.3$

VII. The method of preparing mesitylene di-carbonic acid by oxidizing di-acyl mesitylenes first to the di-glyoxylic acid, isolating this acid and oxidizing further, consumes much time and requires the manipulation of a large quantity of liquid for the preparation of even a few grams of the di-carbonic acid. To avoid these tedious operations an attempt was made to oxidize the diketone directly with acid permanganate solution, but without success, owing to the insolubility of the diketone. The greater part was recovered unchanged.

The following method, however, was found to be advantageous when the isolation of the di-glyoxylic acid was not necessary. Di-acetyl mesitylene was oxidized with alkaline permanganate as before, but in solutions one-half so dilute; *i. e.*, 20 grams of diketone to 4 litres of water and the corresponding quantities of permanganate and alkali. The filtered solution was rendered very slightly acid and evaporated to about one-half its original volume. After cooling, more sulphuric acid was added and then the calculated amount of permanganate (0.61 gram for each gram of di-acetyl mesitylene originally taken). The di-carbonic acid is then separated as before described. The yield is poor, but the saving of time is considerable.

VIII. Direct oxidation of the diketone with permanganate having failed, the action of nitric acid was tried in hopes of obtaining the di-carbonic acid at once from the diketone.

Di-acetyl mesitylene is attacked with great difficulty by dilute nitric acid in a sealed tube. Ordinary concentrated nitric acid dissolves it easily but forms only products that contain nitrogen, and no acids could be obtained in this way. On the other hand, di-chloracetyl mesitylene is oxidized by nitric acid with the greatest ease, both by dilute acid (1:10) in a sealed tube, and by ordinary concentrated acid in an open vessel. The product in both cases is essentially the same, a mixture of acids containing no nitrogen but always containing much chlorine.

The oxidation is most conveniently conducted by dissolving di-chloracetyl mesitylene in a small quantity of concentrated nitric acid in a capacious vessel, and warming gently until action begins. In the cold there is no effect, but when the oxidation is once started it goes on with some violence, and only occasional applications of heat are necessary. After half to three-quarters of an hour, the solution is allowed to cool somewhat and five times its volume of cold water is added. On standing a short time, the copious white precipitate thus formed is filtered and washed with a little water. It consists of at least three acids, all of which crystallize well from hot water, in which they are soluble to different degrees. Organic solvents do not serve as well as water, as they dissolve the acids too readily.

Of the numerous preparations made and purified, the following will serve as types. 30 grams of the crude acid mixture was crystallized from boiling water in 14 fractions. The crystals deposited from the most difficultly soluble fraction were filtered and dried and the filtrate used to redissolve and recrystallize the crystals from the second fraction, whose filtrate, in turn, was used for the third fraction crystals, etc. The last filtrate, containing the most easily soluble acid, was evaporated to dryness on the water bath. This process was repeated six times. The middle fractions showed no tendency to accumulate any one acid, but the end products were distinctly individualized. The head fractions (difficultly soluble) were, therefore, united and purified by E. Fischer's esterification process, as described under mesitylene di-carbonic acid, when practically all the acid was recovered, proving it to be di-ortho-substituted. The tailings were treated in the same way and this acid also proved to be di-ortho-substituted. The headings, on recrystallizing from water, melted at 258°-264°. The tailings, on the other hand, melted at about 280°, and on repeated recrystallization a small amount of this acid was obtained entirely free from chlorine and with a melting point of 294°.

The product of another oxidation, 75 grams of crude acid mixture, was dissolved in a measured quantity of strong soda solution, whose equivalent was known in terms of a solution of hydrochloric acid. The alkaline solution, after filtering, was neutralized in four fractions by adding one-fourth of the calculated amount of hydrochloric acid each time. Each fraction was extracted with ether, and was then recrystallized repeatedly from hot water. The first gave mainly the acid melting up to 265°, the second mainly an acid melting about 248°, while the last two fractions gave only mixtures. Repetition of the process of fractional neutralization did not result in any separation so sharp as could be gotten by crystallizing in fractions from hot water.

In all the separations, more or less pure specimens of the acid melting at about 265° were gotten, and it seems probable that one-third or even one-half of the whole product is this substance. It contains chlorine, but no nitrogen, comes down from hot water in transparent, colorless needles often 3-4 mm. long. The melting point is never perfectly sharp. The best specimen obtained became soft at 259° and was wholly melted at 265°, with slight change of color. The crystals contain no water of crystallization. After two hours in an air bath at 140°, they turn yellow and lose slightly in weight.

The acid gave the following analytical results:

I. 0.10767 gram acid gave 0.05519 gram AgCl.

II. 0.10722 gram acid gave 0.05558 gram AgCl.

III. 0.26991 gram acid gave 0.11451 gram H_2O and 0.52584 gram CO_2.

IV. 0.30445 gram acid gave 0.13108 gram H_2O and 0.59950 gram CO_2.

V. 0.15595 gram acid gave 0.06680 gram H_2O and 0.30683 gram CO_2.

	I.	II.	III.	IV.	V.
Cl	12.67	12.82	..	..	..
C	..	..	53.14	53.70	53.65
H	..	..	4.75	4.78	4.69

The results agree with none of the formulæ à priori possible for the acid. To determine the number of carboxyl groups the two following methods were used:

(*a*) A weighed quantity of the acid was dissolved in water, and to it was added an excess of freshly precipitated, thoroughly washed silver carbonate. The liquid was heated to boiling and quickly filtered, and the washings were added to the filtrate. This latter contained the silver salt of the acid, which is very easily soluble in water and rapidly decomposes. The solution was immediately treated with hydrochloric acid in excess, and the silver chloride thus obtained was filtered and weighed in the usual way.

I. 0.12795 gram acid gave 0.12345 gram AgCl.

II. 0.09479 gram acid gave 0.09227 gram AgCl.

	I.	II.
Ag (per cent in *salt*)	42.07	42.28

A dibasic acid of molecular weight 230 (see below) would require 48.6 per cent Ag in its neutral silver salt.

(*b*) A weighed quantity of acid was dissolved in a measured quantity of standard sodium hydroxide solution and the excess of alkali determined by titration with hydrochloric acid.

1 cc. of NaOH solution contains 0.01712 gram NaOH.

1 cc. of HCl solution ≡ 0.96237 cc. NaOH solution.

I. 0.10262 gram acid in 20 cc. NaOH required 19:07 cc. HCl to neutralize.

∴ there is 0.01604 gram Na in salt of acid.

II. 0.1939 gram acid in 20.20 cc. NaOH required 17.78 cc. HCl to neutralize

∴ there is 0.0304 gram Na in salt of acid.

	I.	II.
Na (per cent in *salt*)	13.52	13.55

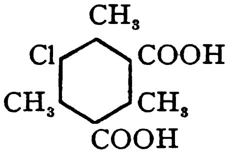
A monobasic acid of molecular weight 230 would have 8.6 per cent of sodium in its salt, a dibasic acid 16.3 per cent of sodium. As the observed molecular weight is probably too low, these results, on the whole, indicate a dibasic acid.

The molecular weight of the acid was determined by the boiling point method, using ether as a solvent.

Wt. solvent.	Wt. subs.	Rise in b. pt.	M.
21.447	0.28310	0.136°	205
22.161	0.71910	0.296°	230

This proves that the acid is not a product of the condensation of two or more molecules of the diketone.

As it was impossible to reconcile these results with any formulæ gotten by oxidizing ketone and methyl groups of di-chloracetyl mesitylene, various attempts were made to determine the structure of this acid chemically. The only one that was of any avail was the action of concentrated aqueous caustic potash. The acid was boiled in this solution for four hours, some of the solution was then acidified with nitric acid and silver nitrate added. *No precipitate* was obtained. The conclusion, therefore, seems justified that the chlorine is not in the side chain. It must then have gone into the unoccupied position of the nucleus. The formula for the acid thus suggested,



calls for the following composition:

Cl	14.6	per cent.
C	54.4	"
H	4.5	"
Ag in salt	47.3	"
Na "	16.1	"

and a molecular weight of 242.5.

The presence of a small amount of a higher oxidation product containing no chlorine would account for the discrepancies between the observed and calculated values. To account for the formation of this acid in the oxidation process, it is necessary to suppose that the chlorine of the di-chloracetyl mesitylene is set free as such to some extent, and that in the nascent state it substitutes in the ring, while the ketone groups are oxidized to carboxyl. There is no case similar to this on record, where the halogen is transported from the side chain into the benzene ring. The idea suggests itself that there may be halogen in the ring of the original chlorketone; but that this is impossible is proved by the fact, as given above, that alkaline permanganate oxidizes the diketone to mesitylene di-glyoxylic acid, and also by a special experiment, as follows: di-chloracetyl mesitylene was boiled with equal parts of alcohol and strong aqueous caustic potash for 24 hours. The alcohol was used to keep the substance in solution. On acidifying with dilute sulphuric acid, a yellow solid was obtained, which was filtered and washed, and which gave *no* qualitative test for halogen. The filtrate, on adding silver nitrate, gave a very copious precipitate of silver chloride. The halogen must, therefore, all be in the side chain.

Of the other acids obtained from the nitric acid oxidation, the acid melting about 248° could not be gotten in homogeneous crystals in quantities sufficient for examination. The easily soluble, high melting acid is probably in large part mesitylene dicarbonic acid, as it has the same crystalline form, the same solubility relations and nearly the same melting point as the pure acid described above. But only very small quantities of it were obtained by the action of nitric acid, so that this method of preparing the acid failed.

CONCLUSION.

The most interesting results of this paper, from a theoretical point of view, are the dissociation constants of the various acids examined, as given in Tables I-X.

Mesitylene mono-glyoxylic acid gives a constant which is comparable with that of phenyl glyoxylic acid found by Bader.[29]

	K.
1. Glyoxylic acid[30] (HCO.COOH)	0.0474
2. Phenyl glyoxylic acid (C_6H_5.CO.COOH)	6.11
3. Mesitylene glyoxylic acid (C_9H_{11}CO.COOH)	5.27

The behavior of mesitylene di-glyoxylic acid is at first sight remarkable; as a dibasic acid it should give values for K that increase with dilution. The reverse is the case. K for $v = 16$ is 6.23 and falls off steadily to 3.50 for $v = 256$. One other instance of such behavior has been observed. Ostwald[31] found that oxalic acid gave a decreasing constant, and he assigned 10 as an approximate value for K. Noticing, then, that mesitylene diglyoxylic acid may be regarded as di-oxalyl mesitylene, the similarity between it and oxalic acid is not surprising; and the cause of the anomalous behavior in both cases must be the same. Further work on the conductivity of ketone acids, especially such as mesoxalic acid, will be necessary before any explanation of these phenomena can be attempted.

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[29] Zeit. physikal. Chem., 6, 314.

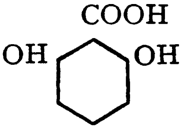
[30] Ostwald, ibid., 3, 188.

[31] Zeit. physikal. Chem., 3, 281.

The conductivity of di-ortho-substituted acids has never been systematically studied; although Ostwald, in the course of his extensive work on the conductivity of organic acids, measured a few di-ortho-substituted oxy-acids of benzene. These were:[32]

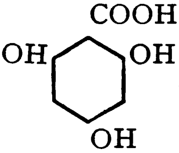
K.

1. β-resorcylic acid,



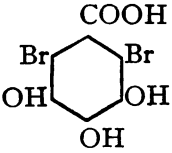
, ... 5.0

2. Phloroglucine carbonic acid,



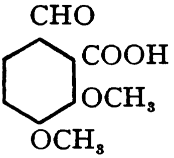
, ... 4.1

3. Di-brom gallic acid,



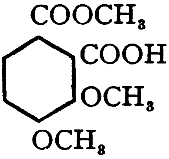
, ... 1.21

4. Opiamic acid,



, ... .088

5. β-hemipinic acid ester,



.... .130

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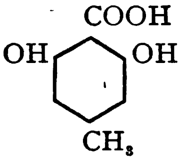
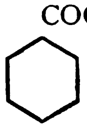
[32] Zeit. physikal. Chem., 3, 418, for list and references.

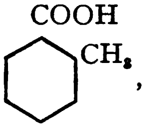
The constants of these acids are all much greater than those of their isomers, not di-ortho-substituted; and Ostwald attributed this to the accumulation of *negative* groups in the ortho position. In fact, finding that para-orsellinic acid, whose orientation was not known, gave a high constant, $K = 4.1$, he assigns it the structure:[33]

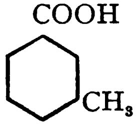


The results of this paper, however, make it probable that it is the ortho, or di-ortho *relation* that affects the dissociation of a carboxyl group, and not the positive or negative character of the group occupying the ortho position. The following comparison shows clearly the intensifying effect of *positive* methyl groups in the ortho position on the conductivity of acids, and at the same time their diminishing effect when in the meta or para positions. The first four acids were measured by Ostwald,[34] who characterizes the behavior of (o) toluic acid as "remarkable," but makes no further comment.

K.

1. Benzoic acid,  0.00600

2. (*o*) Toluic acid,  , ... 0.0120

3. (*m*) Toluic acid,  0.00514

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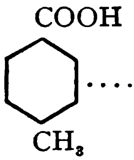
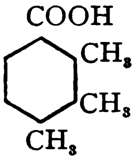
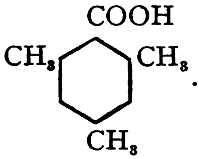
[33] Zeit. physikal. Chem., 3, 254.

[34] Zeit. physikal. Chem., 3, 269-270.

4. (*p*) Toluic acid,  0.00515

5. Prehnitylic acid,  , ... 0.00349

6. Mesitylene carbonic acid,  0.0375

The constant of mesitylene carbonic acid, more than ten times as great as that of its isomer, prehnitylic acid, and three times as great as (*o*) toluic acid, in spite of the greater number of positive groups, is in itself sufficiently remarkable to make a more extended study of the di-ortho relation desirable. And further, the very peculiar behavior of mesitylene di-carbonic acid, in which this di-ortho relation occurs twice, and which gives the decreasing constant (see Table IX) which has been observed so far only in oxalic acid, as described by Ostwald, and in mesitylene diglyoxylic acid, as described in this paper, is entirely inexplicable at present on any grounds, experimental or theoretical. Other acids of the same type must be prepared and studied before any explanation can be attempted.

CONTENTS

I. The Polybasic Acids of Mesitylene. By Mary Bidwell Breed

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